Small angle neutron scattering study of SPBT/PC blends

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Abstract

A series of polymeric blends of semicrystalline sulphonated poly(butylene terephthalate) (SPBT) and amorphous polycarbonate (PC) was studied using small angle neutron scattering. The data has been analysed in terms of Debye–Bueche and two correlation length models. It has been concluded that the blend of unsulphonated PBT/PC is partially miscible, and that temperature, blend composition and particularly sulphonation levels are the principal factors that control its miscibility. The 50/50 blend of 7.9 mol% SPBT/PC is the most miscible at all temperatures studied, and is the most transparent of the blends studied. © 2000 Elsevier Science Ltd. All rights reserved.

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1. Introduction

The objective of this work was to investigate the miscibility of a new polymeric blend of semicrystalline sulphonated poly(butylene terephthalate) (SPBT) and amorphous polycarbonate (PC) (Fig. 1) using small angle neutron scattering (SANS). Blending of polymers is an important route for the creation of materials with improved properties compared to those of their components [1]; it is efficient and usually cheaper than the synthesis of new polymers. Further improvements in miscibility can be achieved by the introduction of ionic groups to one constituent, and subsequently neutralising this group with a metal cation [2–5]. Such chemically altered polymers are referred to as *ionomers*.

One important class, the *random ionomers*, has ionic groups either pendant from the main chain or randomly distributed along the main chain (Fig. 1). Several research groups [6–11] have investigated *ionomer blends* for the last decade. Most of these blends were amorphous mixtures.

Poly(butylene terephthalate) (PBT) is an important engineering thermoplastic because of its attractive mechanical properties, rapid crystallisation rate, and good mouldability. It has been found that PBT has a lower glass-transition temperature (approximately 43°C), a high melting temperature (>220°C), higher crystallisation rate, and lower value of the maximum attainable crystallinity compared to other commercial thermoplastic polyesters (for example poly (ethylene terephthalate)) [12]. PBT also has relatively good solvent resistance, and a high decomposition temperature (approximately 350°C) [13]. However, PBT has some shortcomings such as its relatively low impact strength, low heat deflection temperature, low melt viscosity and poor optical clarity (PBT, being semicrystalline, is opaque). Some of these properties can be improved by copolymerising it with sulphonated PBT. The process of sulphonation destroys this crystallinity, improves miscibility and makes the PBT/SPBT copolymer more transparent [14].

Further improvements come from blending it with PC which, though tough and stable to 300°C, has poor solvent resistance; its T_g is however about 145°C. This has led to commercial interest in such blends. More information about the properties and applications of the PBT and PC can be found in the literature [15–19].

Here we will report work on blends of SPBT/PC: these are new, and the only reference so far is the paper by Nicholson et al. [20] that summarises our thermal analysis, wide-angle X-ray scattering (WAXS) and light microscopy results [21]. Those compositions where fully deuterated polycarbonate (hereafter abbreviated by PC$_d$) was used are new materials [22]. In what follows we give a brief summary of findings most pertinent to this paper. There

$$Na^+ \quad SO_3 \quad O$$
$$-C-\bigcirc-C-O-CH_2-CH_2-CH_2-CH_2-O-$$

(a)

$$O$$
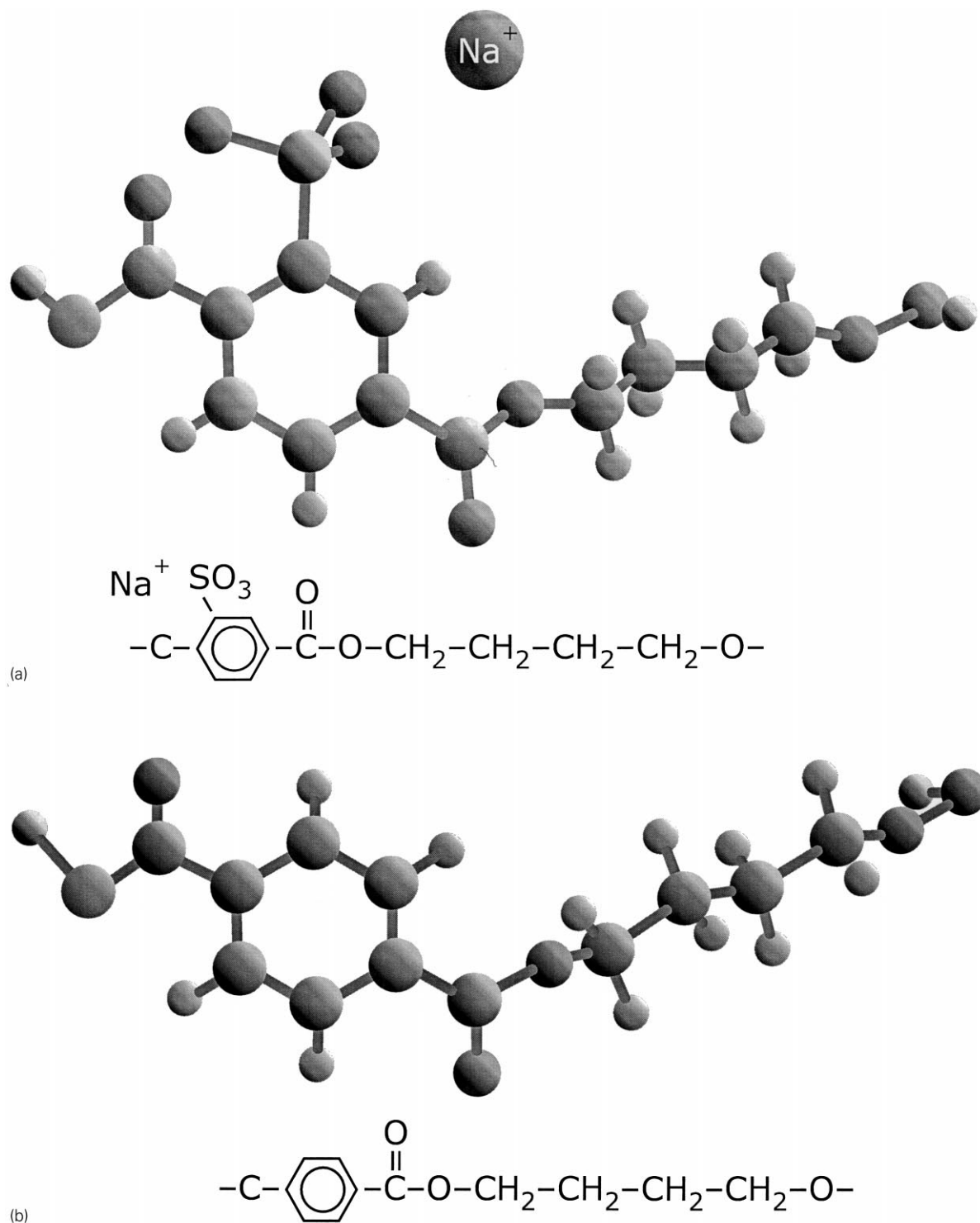$$-C-\bigcirc-C-O-CH_2-CH_2-CH_2-CH_2-O-$$

(b)

Fig. 1. Structure of chemical repeat units of: (a) SPBT, (b) PBT, and (c) PC.

are however several investigations of blends of PBT/PC reported in the literature, and these are referenced and discussed in detail in Ref. [22].

Poly(butylene terephthalate) containing different levels of sulphonated poly(butylene terephthalate) (SPBT) as a comonomer was studied by Gorda and Peiffer with a view to enhance miscibility [14]. They investigated the morphology and mechanical properties of SPBT and its unfunctionalised analogue PBT by wide-angle X-ray scattering (WAXS), polarised light microscopy and small angle light scattering (SALS). The type of spherulitic structure found in these polyesters depends upon the sulphonation level [21],
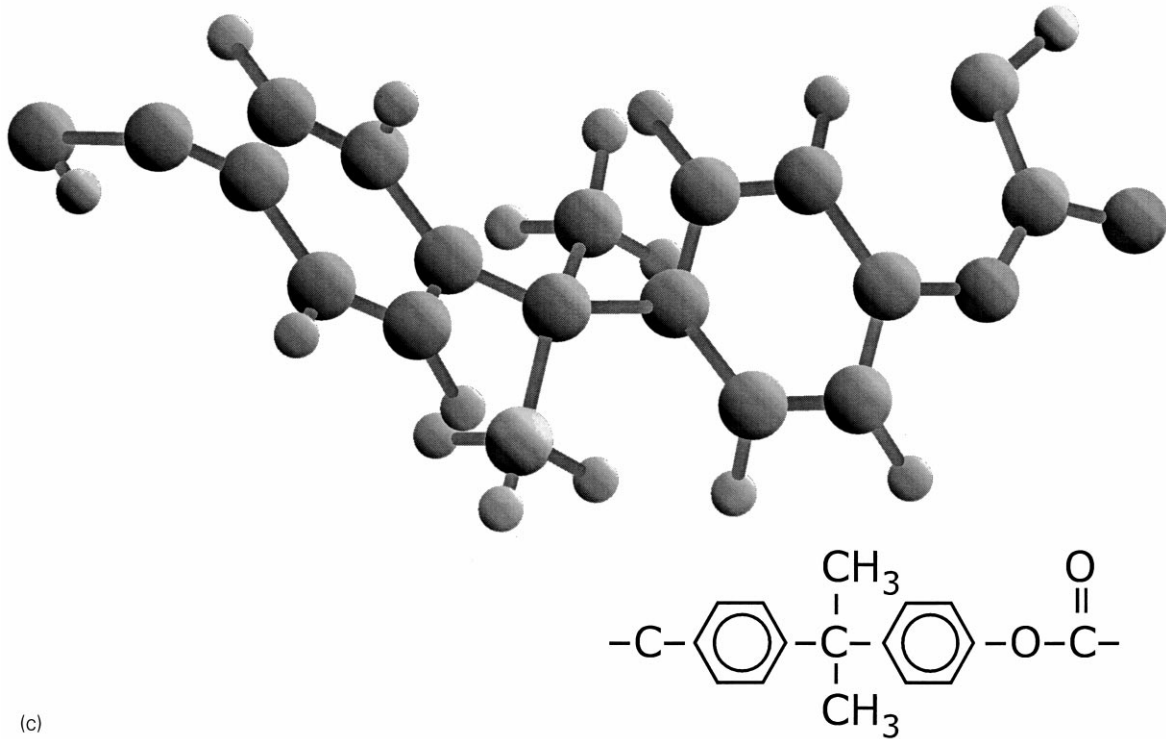
(c)

Fig. 1. (*continued*)

as does the degree of crystallinity; the latter decreases with ionic content while the spherulite radius remains relatively constant. It was demonstrated that increasing the level of the sodium sulphonated polybutylene terephthalate comonomer leads to enhanced optical clarity, as expected, principally due to the decrease in crystallinity with increasing ionic comonomer content. Gorda and Peiffer [14] have shown that increasing the sulphonate content enhanced the maximum extension at failure but resulted in a decrease in the tensile strength and overall modulus. This enhanced ducti-

lity under ambient conditions was attributed to the loss of crystalline texture.

Further studies by Nicholson et al. [20] of PBT, SPBT and their blends with PC showed that the trend of decreasing crystallinity with increasing sulphonation level was in agreement with both the DSC and X-ray results. The PBT and 4.9 mol% SPBT showed nearly identical behaviour, whereas SPBT with a sulphonation level of more than 7 mol% showed disorder, visible as a broadening of X-ray diffraction peaks. The melt blends 7.9 and 11.1 mol%

Table 1
Characteristics of the samples

| Sample	Blend composition (% w/w)	Density (g cm^{-3})	Scattering length density (/10^{10} cm^{-2})	Scattering contrast per unit volume (/10^{20} cm^{-4})
PC$_d$	100	1.2	5.855	
PBT	100	1.31	2.083	
3.5 mol% SPBT		1.309	2.082	
7.9 mol% SPBT		1.308	2.082	
11.1 mol% SPBT		1.307	2.081	
PBT/PC$_d$	75/25[a]			
PBT/PC$_d$	50/50			14.220
3.5 mol% SPBT/PC$_d$	75/25			
3.5 mol% SPBT/PC$_d$	50/50			14.240
7.9 mol% SPBT/PC$_d$	75/25			
7.9 mol% SPBT/PC$_d$	50/50			14.223
11.1 mol% SPBT/PC$_d$	90/10[a]			
11.1 mol% SPBT/PC$_d$	75/25[a]			14.230

[a] Samples used in the preliminary study [20].
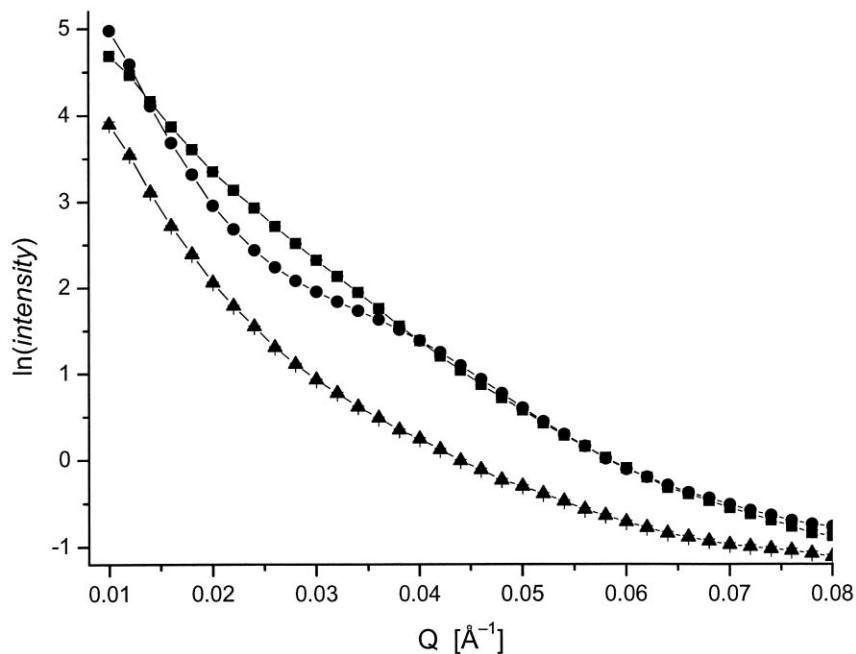
Fig. 2. SANS patterns obtained at 215°C from 50/50 blends of: PBT/PC$_d$ (■), 3.5 mol% SPBT/PC$_d$ (●), and 7.9 mol% SPBT/PC$_d$ (▲).

SPBT/PC showed partial miscibility. Light microscopy experiments on the blends indicated that the bulky sulphonate groups reside in the amorphous phase, and the partially crystalline SPBT chains remain in the other phase. The dependence of glass transition temperatures upon the mass fraction of amorphous SPBT indicated that the optimal miscibility lies somewhere between 7.9 and 11.1 mol%.

The present study is the continuation of these studies using small angle neutron scattering (SANS). The data obtained on these blends is analysed in terms of Debye–Bueche and two-correlation length models. The parameters calculated from these models, the short and long range correlation lengths, the second derivative of the Gibbs free energy of mixing and the polymer–polymer interaction parameter χ, are used to explain the miscibility, phase
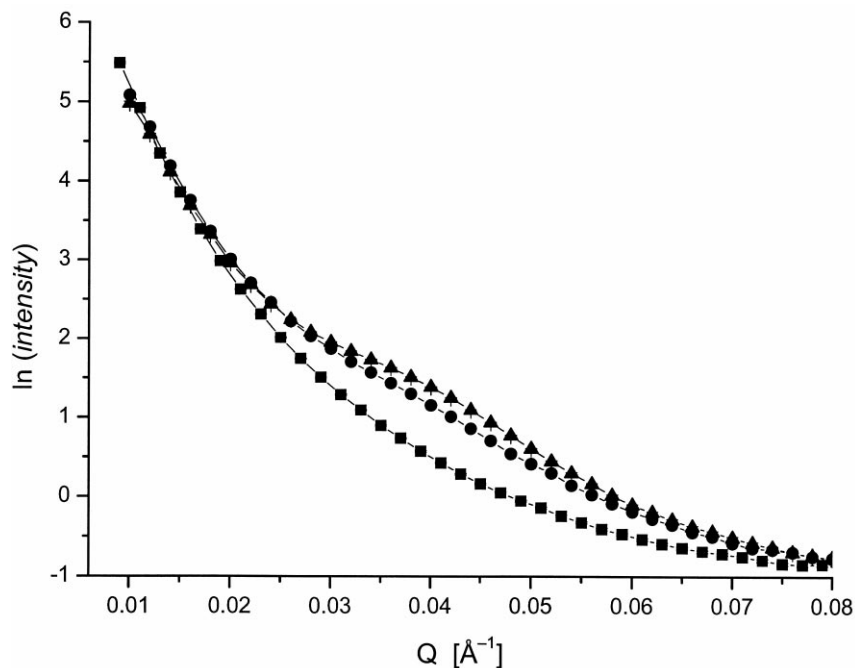

Fig. 3. SANS patterns obtained from the 50/50 blend of 3.5 mol% SPBT/PC$_d$ at temperatures of: 165°C (■), 200°C (●), and 215°C (▲).
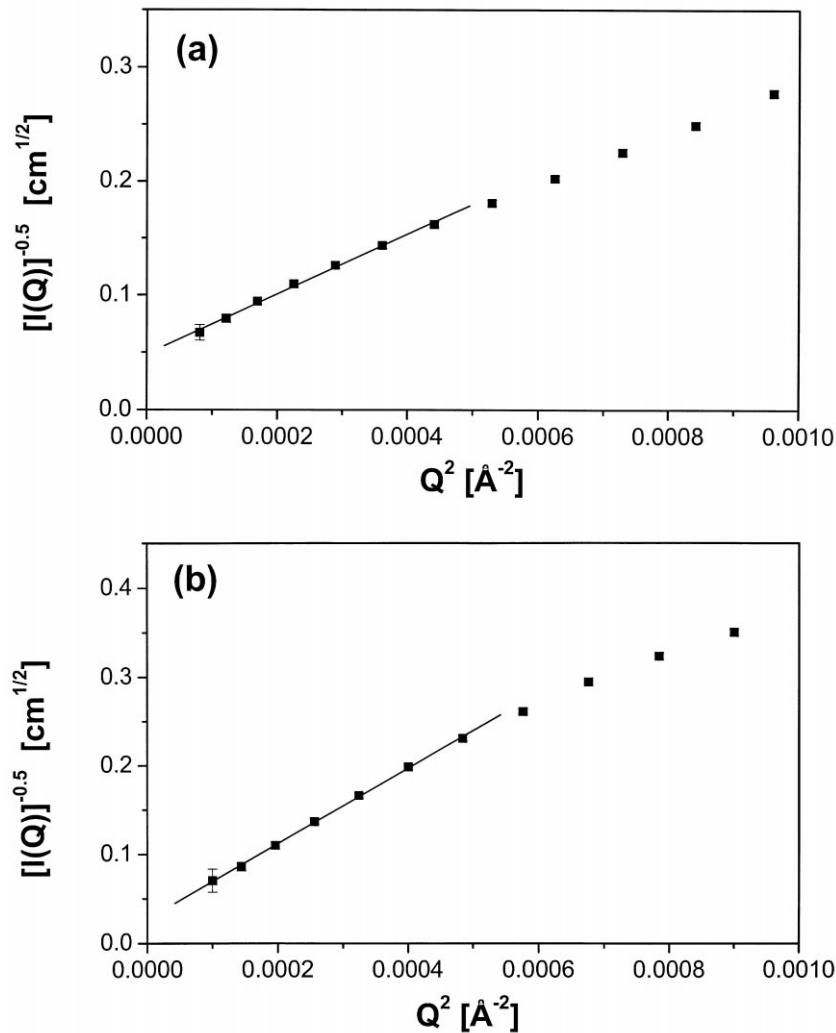
Fig. 4. SANS patterns, obtained at 200°C and plotted according to Eq. (3), the Debye–Bueche model, from 50/50 blends of: (a) PBT/PC$_d$, (b) 3.5 mol% SPBT/PC$_d$, and (c) 7.9 mol% SPBT/PC$_d$. The solid line is the best linear fit to the data.

separation, crystallinity and improved properties (like processing and optical clarity) of SPBT/PC$_d$ blends. The results obtained from the SANS experiments are shown to be consistent with those from the previous study [20,21].

2. Experimental

Sodium sulphonated poly(butylene terephthalate) with sulphonation levels 3.5, 7.9 and 11.1 mol%; and poly(butylene terephthalate) were supplied by Exxon Chemicals, USA. These materials were the same as those used by Gorda and Peiffer [14]. They noted that M_w and the density should be the same as that in Ref. [23], where $M_w = 55,000$ g/mol, because the PBT was synthesised under the same controlled conditions. The density of SPBT used here is somewhat smaller than their estimate for PBT, 1.31 g/cm^3, because the ionic content decreases the crystallinity of PBT and hence its density. Dr Wagner of the Max Planck

Institute, Mainz, Germany, kindly donated the deuterated PC (hereafter abbreviated as PC$_d$). The M_w of the PC$_d$ was 40,000 g/mol and its density 1.2 g/cm^3. Some characteristic quantities for the samples used are given in Table 1.

3. Preparation of the blends

The blends of PBT, 3.5, 7.9 and 11.1 mol% SPBT with PC$_d$ were initially prepared by dissolving these individual components in a mixture 40/60 (% w/w) phenol/tetrachloroethane to yield 2% (w/v) solutions. The blends listed in Table 1 were then formed by mixing appropriate volumes of the solutions. The blended solutions were put in sealed bottles and left for three days on a stirrer-hotplate to ensure proper mixing, after which time the samples were cast in small (Teflon coated) open containers to air dry for one week at room temperature. Samples of pure PBT and pure PC$_d$ were also dissolved and cast for comparison. Final
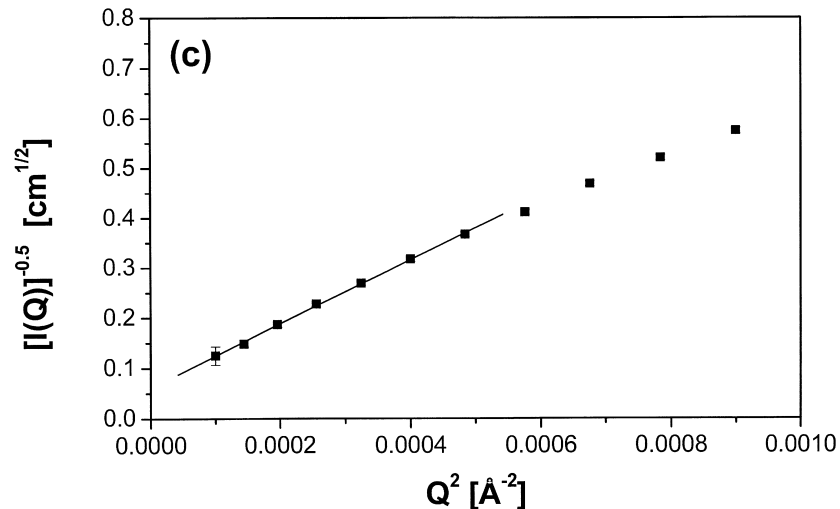
Fig. 4. (*continued*)

drying of samples was accomplished under vacuum at 80°C for 7 h in order to remove water vapour and remaining solvent. IR spectroscopy measurements showed no evidence of the residual solvent after this drying procedure. The samples were then melt pressed at ~227°C in air.

4. SANS experiment

SANS experiments were performed on the LOQ small-angle diffractometer ([24]; see also http://www.isis.rl.ac.uk/LargeScale/LOQ/loq.htm) at the ISIS Spallation Neutron Source, Oxfordshire, UK. This is a "white beam" time-of-flight instrument equipped with fixed low and high angle two-dimensional detectors giving a simultaneous and continuous scattering vector range of $0.0085 < Q < 1.52 \, \text{Å}^{-1}$.

The samples were mounted on a nine-position brass rack with an integral high power cartridge heater atop a computer-controlled translation stage. Each position could contain one sample, encased in a cylindrical brass holder and held between a PTFE washer by two 1-mm quartz windows and a threaded locking ring. A thermocouple was placed in direct contact with a sample holder for monitoring of the sample temperature. The incident neutron beam was collimated to 8 mm in diameter. Data were recorded at temperatures of 30, 160, 165, 200 and 215°C. Time of collection of each dataset varied from one and a half to two and a half hours.
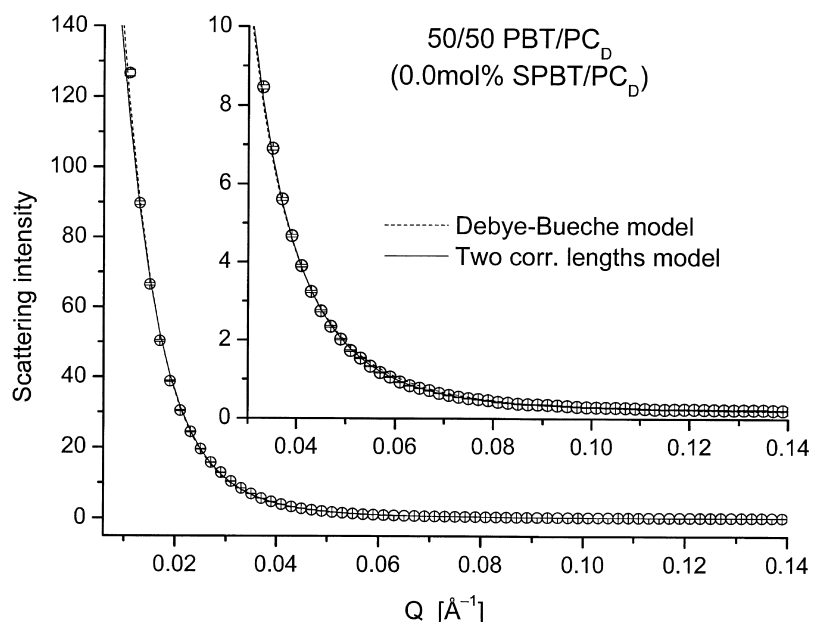

Fig. 5. SANS pattern from the 50/50 blend of PBT/PC$_d$ at 200°C. The inset figure shows a close-up of the *I(Q)* plot for small intensities.
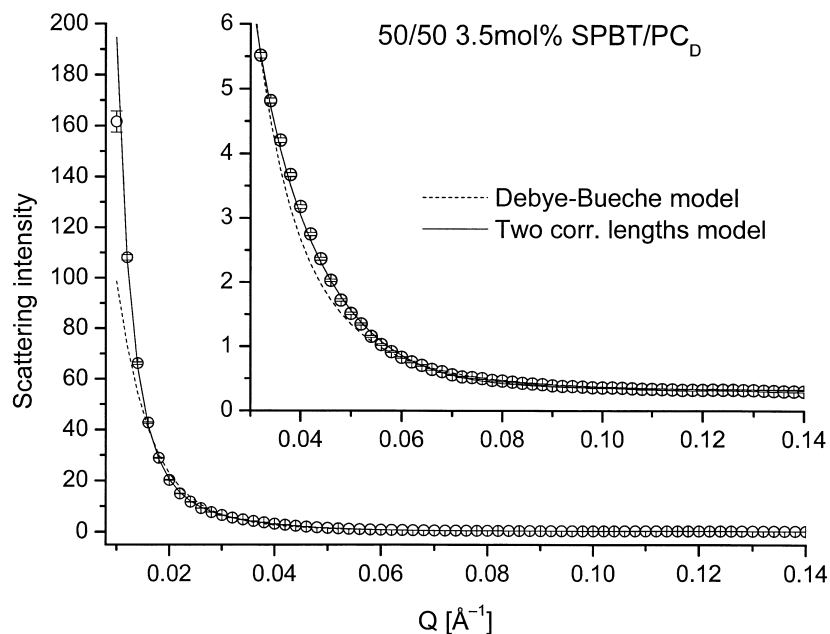
Fig. 6. SANS pattern from the 50/50 blend of 3.5 mol% SPBT/PC$_d$ at 200°C. The inset figure shows a close-up of the I(Q) plot for small intensities.

Each raw scattering dataset was corrected for the sample transmission and background scattering and converted to scattering cross-section data using the instrument-specific software [25]. These data were placed on an absolute scale (cm^{-1}) using the scattering from a standard sample (a solid blend of hydrogenous and perdeuterated polystyrene) in accordance with established procedures [26].

The neutron scattering length densities, ρ, of the polymers tabulated in Table 1 were calculated according to the expression

$$\rho = b\left(\frac{DN_A}{M_m}\right) \tag{1}$$

where b is the *sum* of the atomic scattering lengths in the repeat unit [27], D is the bulk polymer density (given in Table 1), N_A is Avogadro's number and M_m is the molar mass of the repeat unit. The scattering contrast per unit
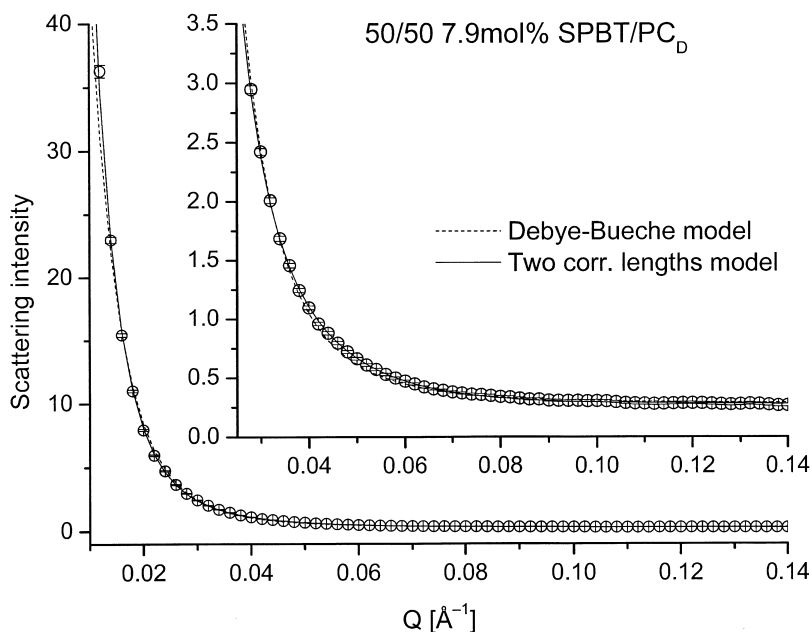

Fig. 7. SANS pattern from the 50/50 blend of 7.9 mol% SPBT/PC$_d$ at 200°C. The inset figure shows a close-up of the *I(Q)* plot for small intensities.

Table 2
Parameters obtained from the Debye–Bueche model fits to the data

Sample	Blend composition (% w/w)	Temperature (°C)	A (cm^{-1})	a_c (Å)	$\bar{L}_1$ (Å)	$\bar{L}_2$ (Å)	$(\partial^2 \Delta G_{mix}/\partial \phi^2)/10^{-3}$	$\chi_{1,2}/10^{-3}$
PBT/PC$_d$	50/50	165	332	71 ± 1	124	165	1.19	12.32
PBT/PC$_d$	50/50	200	290	68 ± 1	119	158	1.37	12.24
PBT/PC$_d$	50/50	215	199	63 ± 1	110	146	1.98	11.93
3.5 mol% SPBT/PC$_d$	75/25	215	5275	180 ± 3	594	258	0.08	20.22

volume of a polymer blend, $(\Delta\rho)^2$, is then

$$(\Delta\rho)^2 = (\rho_1 - \rho_2)^2 = \left(\frac{b_1 - \beta b_2}{V_1}\right)^2 \tag{2}$$

where $\beta = (V_1/V_2)$, the ratio of the molar volumes, and the subscripts 1 and 2 refer to the PBT or SPBT, and PC$_d$, respectively.

5. Results and discussion

Typical SANS patterns obtained from 50/50 blends of PBT/PC$_d$, 3.5 and 7.9 mol% SPBT/PC$_d$ at 215°C are shown in Fig. 2, and Fig. 3 shows the scattering from the 50/50 3.5 mol% SPBT/PC$_d$ blend as a function of temperature.

Some of the scattering patterns exhibit a broad shoulder around $Q = 0.04$ Å^{-1}. We attribute the low-Q scattering to the presence of crystalline domains within the blend. This assertion is based on the observation that the scattering intensity decreases as the degree of sulphonation increases and as the temperature is raised to the melting temperature of PBT (determined to be 217°C for the 3.5 mol% SPBT/PC sample [19]).

If the blends can be described as random two phase systems then it should be possible to model the SANS

data using the *Debye–Bueche* expression

$$I(Q) = \frac{A}{(1 + Q^2 a_c^2)^2} \tag{3}$$

where a_c is the corresponding correlation length of the blend, which may be interpreted as the size of the density fluctuations, and the parameter A — the zero-angle scattering — is related to the thermodynamic properties of the blend. This aspect is discussed later in more detail.

Examples of data linearised according to this model are shown in Fig. 4. These show that the data are only linear over a limited Q^2 range, which varies from blend to blend. Outside this range the plots are non-linear. This behaviour is typical of blends that are only partially miscible, but not completely phase separated [28]. A single correlation length cannot describe scattering from such blends.

In such instances one can use a *two correlation length model* to account for both the short range (a_1) and long range (a_2) correlation lengths [29,30]:

$$I(Q) = \frac{A_1}{(1 + Q^2 a_1^2)^2} + A_2 \exp\left(-\frac{Q^2 a_2^2}{4}\right) \tag{4}$$

The coefficients A_1 and A_2 then relate the relative contributions of amorphous and crystalline behaviour.

In Figs. 5–7 the data used to generate Fig. 4 has been replotted as $I(Q)$ vs Q and model fits to Eq. (4) have been

Table 3
Parameters obtained from the two-correlation length model fits to the data

Sample	Blend composition (% w/w)	Temperature (°C)	A_1 (cm^{-1})	A_2 (cm^{-1})	a_1 (Å)	a_2 (Å)	$(\partial^2 \Delta G_{mix}/\partial \phi^2)/10^{-3}$	$\chi_{1,2}/10^{-3}$
PBT/PC$_d$	75/25	160[a]	481	0.15	11 ± 36	73 ± 1.4	0.83	20.11
3.5 mol% SPBT/PC$_d$	75/25	165	16869	8.72	63 ± 1	237 ± 22	0.02	20.25
3.5 mol% SPBT/PC$_d$	75/25	200	21143	11.58	65 ± 1	256 ± 29	0.02	20.25
3.5 mol% SPBT/PC$_d$	50/50	165	4292	0.53	45 ± 1	196 ± 3	0.09	13.95
3.5 mol% SPBT/PC$_d$	50/50	200	5870	6.11	57 ± 1	213 ± 18	0.07	13.97
3.5 mol% SPBT/PC$_d$	50/50	215	29092	9.27	56 ± 1	344 ± 141	0.01	13.99
7.9 mol% SPBT/PC$_d$	75/25	30	498	0.15	36 ± 2	138 ± 2	0.82	19.56
7.9 mol% SPBT/PC$_d$	75/25	160[a]	5384	1.66	51 ± 1	227 ± 15	0.08	19.93
7.9 mol% SPBT/PC$_d$	75/25	215	481	0.99	51 ± 1	137 ± 3	0.85	19.54
7.9 mol% SPBT/PC$_d$	50/50	165	497	0.31	39 ± 1	141 ± 1	0.83	12.34
7.9 mol% SPBT/PC$_d$	50/50	200	265	0.58	47 ± 1	112 ± 2	1.55	11.97
7.9 mol% SPBT/PC$_d$	50/50	215	322	1.34	51 ± 1	122 ± 2	1.27	12.11
11.1 mol% SPBT/PC$_d$	90/10	30	476	1.31	58 ± 1	130 ± 4	0.88	44.25
11.1 mol% SPBT/PC$_d$	90/10	160[a]	618	0.94	48 ± 2	192 ± 8	0.68	44.35
11.1 mol% SPBT/PC$_d$	75/25	160[a]	2220	0.75	53 ± 1.5	145 ± 4	0.19	19.66

[a] Samples used in the preliminary study [20].

used to extract both the short and long range correlation lengths and the two intensity coefficients.

We have found that the SANS data for the 50/50 blend of PBT/PC$_d$ measured at temperatures of 165, 200 and 215°C are only fitted well by the simple Debye–Bueche model with a flat background. This appears to be a general rule: the Debye–Bueche model proves satisfactory for all investigated blends with unsulphonated PBT, at all temperatures studied. The SANS data from all of the other SPBT/PC blends fit much better to the two correlation length model.

5.1. Debye–Bueche model

The values of the zero angle scattering, A, and the correlation length, a_c, are noted in Table 2. The value of A for the 75/25 blend of 3.5 mol% SPBT/PC$_d$ is very high, and can be linked to the presence of large crystallites. For the PBT/PC$_d$ blend A decreases with increasing temperature. This effect is not easily interpreted, since A is a product of the correlation length parameter, a_c, to the third power, and volume fractions of two phases. Therefore the decrease in the correlation length is likely to influence A strongly. The parameter a_c is also the measure of the size of the heterogeneity ([29], Eq. (2)), and the decrease in a_c implies diminishing size of the heterogeneity. Upon these assumptions the data indicates melting of the crystallites with increasing temperature (which is why the size of heterogeneity decreases).

Knowing the correlation length, the *average* transversal lengths through the two phases can be calculated. Hence $\bar{L}_1 = (a_c/\phi_1)$ for the crystalline phase and $\bar{L}_2 = (a_c/\phi_2)$ for the amorphous phase, where ϕ_i is the composition [10,31–33]. These average transversal lengths are also listed in Table 2. The degree of crystallinity can then be estimated as $\bar{L}_1 = [\bar{L}_1/(\bar{L}_1 + \bar{L}_2)]$, giving 42% for the 50/50 blend of PBT/PC$_d$, which is consistent with DSC results giving 41% [20]. For the 75/25 blend of 3.5 mol% SPBT/PC$_d$ the degree of crystallinity is found to be 69.7%. The DSC results for this sample were inconclusive.

A short digression on the relationship between the crystallinity and the degree of sulphonation is in order here. We have previously observed in amorphous polystyrene that a small amount of sulphonation *increases the short range order prior to its destruction* upon further sulphonation. The best ordering was observed for 0.45 mol% sodium sulphonated polystyrene [34]. Similar effects may take place for SPBT, with an important difference: that the destruction of "crystallites" in SPBT is much more gradual than the destruction of the short range order observed in polystyrene. A physical picture would be that of large SO_3^- groups causing a local rearrangement of a few atoms. It is then not unreasonable to suppose that there exists one, most spatially efficient, conformation, with the higher degree of crystallinity than that of unsulphonated sample.

The degree of miscibility between the phases can be quantified through the second derivative of the Gibbs free energy of mixing, $\partial^2 \Delta G_{mix}/\partial \phi^2$, and the interaction parameter, $\chi_{1,2}$, calculated from [35]

$$\frac{V}{I(0)} = \frac{1}{\nu_0 \left(\frac{b_1 - \beta b_2}{V_1} \right)^2} \left[\frac{1}{\phi_1 N_1} + \frac{1}{\phi_2 N_2} - 2\chi_{1,2} \right]$$

$$= \frac{1}{\nu_0 \left(\frac{b_1 - \beta b_2}{V_1} \right)^2} \frac{\partial^2 G/\partial \phi^2}{k_B T} \tag{5}$$

where ν_0 is the reference volume. These data are also shown in Table 2.

The values of $\partial^2 \Delta G_{mix}/\partial \phi^2$ increase with increasing temperature. The values of $\chi_{1,2}$ are all positive and decrease with increasing temperature. Together, these data show that with increasing temperature the crystallites start to melt, the crystallinity decreases and the polymers begin to mix. The melting temperature of the 50/50 blend of PBT/PC$_d$ was measured to be 219°C by DSC [20], whereas the SANS experiments were conducted at temperatures up to 215°C.

5.2. Second derivative of the Gibbs free energy of mixing and interaction parameter $\chi_{1,2}$

From the thermodynamical point of view, the Flory–Huggins interaction parameter $\chi_{1,2}$ is crucial for determination of the blend miscibility [36]. This, and the second derivative of Gibbs free energy of mixing, can be calculated from the scattering intensity at zero angle, obtained from both the Debye–Bueche model (where $I(0) = A$) and the two correlation length model below (where $I(0) = A_1 + A_2$) via Eq. (6). The values of $\partial^2 \Delta G_{mix}/\partial \phi^2$ and $\chi_{1,2}$ derived are presented in Tables 2 and 3.

For the system to be miscible the well-known stability condition states that

$$\partial^2 \Delta G_{mix}/\partial \phi^2 \geq 0 \tag{6}$$

This condition is met by the blends of PBT/PC$_d$ and SPBT/PC$_d$, although the values of $\partial^2 \Delta G_{mix}/\partial \phi^2$ are very small. The values for PBT/PC$_d$ are higher than those obtained for the 3.5 mol% SPBT/PC$_d$ blend. The transparent blend, 7.9 mol% SPBT/PC$_d$, has the highest values of $\partial^2 \Delta G_{mix}/\partial \phi^2$. Moreover, at the temperature at which the experiment was conducted, composition and sulphonation level have a significant influence: with increasing temperature the value of $\partial^2 \Delta G_{mix}/\partial \phi^2$ increases. It also increases with the increasing PC content — the highest value of $\partial^2 \Delta G_{mix}/\partial \phi^2$ (1.55×10^{-3} for 50/50 composition) is obtained for 7.9 mol% SPBT/PC$_d$.

The negative values of $\chi_{1,2}$ indicate that the system is miscible [36]. Interactions between the constituent polymers will be strong if the values of $\chi_{1,2}$ are large and negative. Our results indicate that these blends are partially miscible and that the constituent polymers only interact weakly.
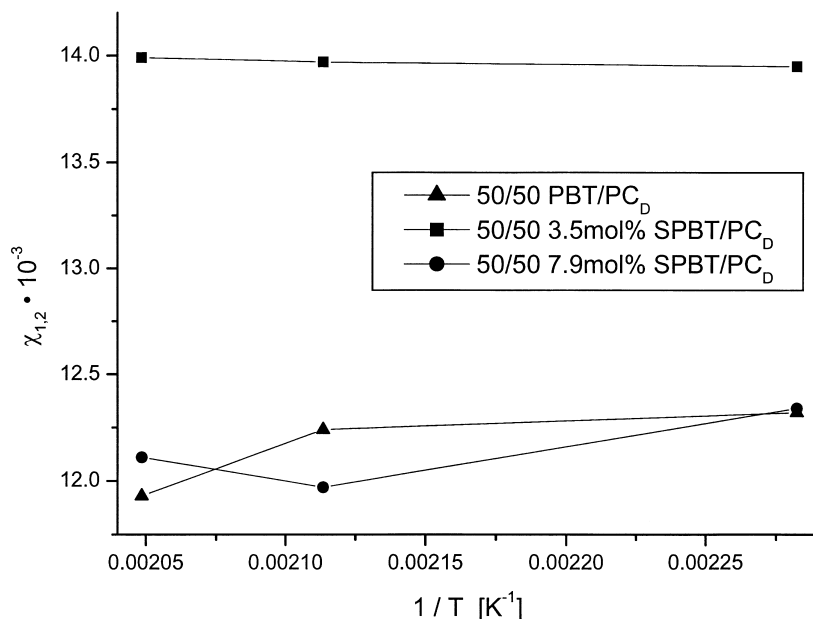
Fig. 8. The temperature dependence of the interaction parameter $\chi_{1,2}$ for 50/50 blends of: PBT/PC$_d$ (▲), 3.5 mol% SPBT/PC$_d$ (■), and 7.9 mol% SPBT/PC$_d$ (●). The lines are guides for the eye.

5.3. The two-correlation length model

The values of coefficients A_1 and A_2 are lower for the 7.9 mol% SPBT/PC$_d$ blend than they are for the 3.5 mol% SPBT/PC$_d$ blend. Again, if one assumes that the intensity at low Q values is predominantly due to the scattering from crystallites then the 7.9 mol% SPBT/PC$_d$ has lower crystallinity than the 3.5 mol% SPBT/PC$_d$ blend. However, there may be a contribution to the low-Q scattering from voids

and impurities due to the sample preparation procedure, which cannot be assessed in a quantitative way. In addition, an interchange reaction termed *transesterification* is known to occur in these blends [37–39], and its impact on data analysis is discussed below.

The short range correlation length (the size of the density fluctuation) for all the 75/25 blends of SPBT/PC$_d$ is in general longer than that obtained for the 50/50 blends at all temperatures above room temperature. This clearly
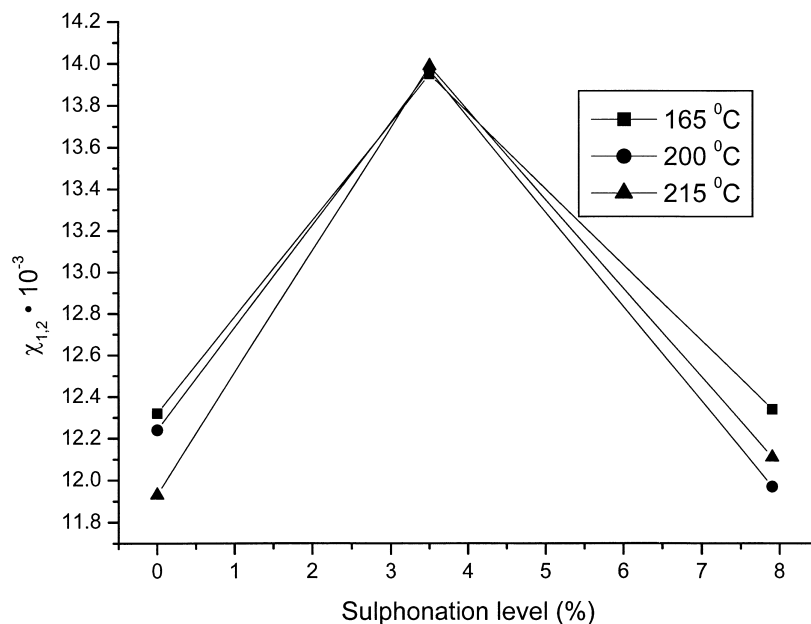

Fig. 9. The dependence of the interaction parameter $\chi_{1,2}$ on sulphonation level for 50/50 blends with PC$_d$ of PBT, 3.5 mol% SPBT, and 7.9 mol% SPBT, at temperatures of: 165°C (■), 200°C (●), and 215°C (▲). The lines are guides for the eye.

shows that the size of the density fluctuation decreases if the amount of polycarbonate in the blend is increased. There is also an increase in a_1 with an increase in the annealing temperature. This is no doubt related to enhanced mixing. The values of a_1 for the 50/50 blend of 7.9 mol% SPBT/PC$_d$ are lower than those obtained for the same 3.5 mol% SPBT/PC$_d$ blend. This points to the unusually high degree of crystallinity of the 3.5 mol% sample (as explained above), which remains high even after mixing with the amorphous PC.

The long-range correlation length a_2 displays very similar behaviour to the short-range correlation length, although curiously the value of a_2 for the 50/50 blend of 7.9 mol% SPBT/PC$_d$ decreases with increasing temperature. On the basis of the existing data, it is not possible to tell whether this is a significant trend, or not.

The correlation length is a statistical measure whose magnitude is dependent on both the sample geometry and distribution of the heterogeneity. Therefore, the interpretation of the short and long range correlation lengths is not easy due to the partial miscibility of these blends. It is however reasonable to assume here that short range correlation lengths of order of tens of Ångstroms is the distance between SPBT and PC in the amorphous phase, or some local clusters in amorphous phase. On the other hand, the long range correlation length, which ranges from about 70–230 Å, might then correlate with the size of PBT crystallites. This assumption is based upon previous X-ray and light microscopy measurements [20] that show the existence of two correlation lengths, one about 100, and the other about 200 Å. Spherulites, 30–50 μm across, were also visible. These would not be visible by SANS, but may contribute to the excess scattering intensity at low values of the scattering vector Q.

At 160°C the average values of $\chi_{1,2}$ derived from the 75/25 blend data are positive and marginally smaller for 11.1 mol% SPBT/PC$_d$ blends than they are for 7.9 mol% SPBT/PC$_d$ blends or PBT/PC$_d$ blends. At higher temperatures, comparison of the $\chi_{1,2}$ values from the 75/25 blends of 3.5 mol% SPBT/PC$_d$ and 7.9 mol% SPBT/PC$_d$ shows that it is the latter which is lower.

The effect of the blend composition on the values of the interaction parameter is evident from the results listed in Table 3. A 50/50 blend has lower values of $\chi_{1,2}$ than corresponding 75/25 blends. This is true of blends that contain 3.5 or 7.9 mol% SPBT and is independent of temperature. Looking at the data for the 50/50 blends of unsulphonated and sulphonated PBT with PC$_d$ (Tables 2 and 3) gives some idea about how $\chi_{1,2}$ changes with temperature. This is also shown in Fig. 8. Interestingly there is a greater similarity of $\chi_{1,2}$ values between the 7.9 mol% SPBT/PC$_d$ blend and the *unsulphonated* PBT/PC$_d$ blend than there is between the former and the 3.5 mol% SPBT/PC$_d$ blend. This result, which is consistent with the results obtained from DSC and optical microscopy techniques [20,21], is presented in Fig. 9. It is clear that the 3.5 mol% blend is the least miscible of all the blends studied, at every temperature.

To quote from Nicholson et al. [20]: "The SPBT chains, with randomly distributed, bulky sulphonate groups, are assumed to form the amorphous phase. The light micrographs indicate that phases with two different levels of sulphonation are formed, namely unsulphonated, which is crystalline, and a sulphonate-containing amorphous phase. This non-random distribution of the sulphonate groups between the two phases could be the reason for the appearance of isolated spherulites". Hence, one could speculate that it is the amorphous PBT/SPBT phase that is mixing with PC. This argument is indirectly supported by Marr [30] who compared the long correlation length a_2 to the size of polymer molecules within the blend. He studied a system comprising a semi-crystalline polyethylene blended with a branched ethylene/ethyl acrylate copolymer. The data indicated that domains described by the a_2 parameter consist of very few polymer molecules. This would, by analogy, be the case with the PBT crystallites in this work.

A note on the effects of transesterification is in order here. Transesterification of a main-chain aromatic polyester results in a change of a degree of polymerisation of the original polymer. This in turn modifies the signal obtained from SANS. A recent study by Backsona et al. on poly-(ethylene terephtalate)–poly(butylene terephtalate) mixtures gives a quantitative measure of this reaction in terms of rate constants and relative changes in the degree of polymerisation with time and temperature [37]. A comparison of times (1.5–2.5 h) and temperatures (highest 488 K) used in our measurements with those recorded in Ref. [37] allows for a good estimate of the influence of transesterification on SANS data in our case. In the worst case, i.e. the highest T and the longest time we obtain a coefficient (−0.2) for the relative change in the degree of polymerisation, thus M_w. This means that ca. 80% of the original polymer is still left intact (Fig. 5, [37]). Since most experiments were done at half the length of this time and at lower temperatures, we can reasonably expect that the change in M_w is of the order of 10%. Moreover, the melting temperature of SPBT with the degrees of sulphonation studied by us [20] is about ten degrees lower than the highest temperature investigated in this paper. Hence, we expect that the competition between crystallisation and transesterification will favour the former and the rate of the latter will be small. This hypothesis was proposed for PBT by Backsona et al. [37] for $T = 476$ K, which is close to our measurement.

6. Conclusions

In this paper, a quantitative description of the miscibility of the SPBT/PC$_d$ blends has been presented. The data analysis indicates that the blend of PBT/PC$_d$ is partially miscible, and that temperature, blend composition and particularly sulphonation levels are the principal factors that control its miscibility. The 50/50 blend of 7.9 mol% SPBT/PC$_d$ is the most miscible at all temperatures studied. An important

point here is the low scattering as $Q \rightarrow 0$, pointing to a relative absence of aggregates. The 75/25 blend of 3.5 mol% SPBT/PC$_d$ is the least miscible. The increase in miscibility (or reduction in crystallinity) can therefore be confidently ascribed to the increase in the degree of sulphonation of PBT, and to the amount of PC in the blend.

The values of $\bar{L}_1$ (crystalline phase size) and $\bar{L}_2$ (amorphous phase size) showed that the proportion of crystalline phase in the PBT/PC$_d$ blend is consistent with the results obtained from DSC [20]. The amount of the amorphous phase is greater than the amount of crystalline phase. We have found that for the same blend composition, but different sulphonation levels and temperatures, there was a uniform change in the correlation lengths. For example, the 50/50 blend of 3.5 mol% SPBT/PC$_d$ has higher a_1 and a_2 values compared to the 50/50 7.9 mol% SPBT/PC$_d$ blend. The a_1 and a_2 values in 3.5 mol% SPBT/PC$_d$ generally increase with temperature, whereas in the 7.9 mol% SPBT/PC$_d$ blend only a_1 increases (a_2 follows a less obvious trend).

Detailed examination of the values of $\chi_{1,2}$ obtained for 50/50 blends of PBT/PC$_d$ and SPBT/PC$_d$ at temperatures 165, 200 and 215°C shows that the unsulphonated blends have lower (positive) values of $\chi_{1,2}$ than the 3.5 mol% sulphonated blends. Despite this, the 50/50 blend of 7.9 mol% SPBT/PC$_d$ has the lowest overall $\chi_{1,2}$ values. This indicates that this blend is more miscible than other blends.

The values of the second derivative of the Gibbs free energy are, on average, the largest for the blend of 7.9 mol% SPBT/PC$_d$. However, the blend of unsulphonated PBT/PC$_d$ as well as 90/10 blend of 11.1 mol% SPBT/PC$_d$ also show relatively high values of $\partial^2 \Delta G_{mix}/\partial \phi^2$, namely 0.83×10^{-3} and 0.88×10^{-3}, respectively (Table 3). On the other hand, detailed examination of the values of $\chi_{1,2}$ obtained for 50/50 blends of PBT/PC$_d$ and SPBT/PC$_d$ at temperatures 165, 200 and 215°C, shows that although the unsulphonated blends have lower (positive) values of $\chi_{1,2}$ than the 3.5 mol% sulphonated blends, the 50/50 blend of 7.9 mol% SPBT/PC$_d$ has the lowest overall $\chi_{1,2}$ values. Used in conjunction, these observations lead us to conclude that the latter blend is more miscible than the other blends investigated.

In summary, the optimal composition of the blend with respect to miscibility (and optical clarity) is 50/50, with a sulphonation level of 7.9 mol%.

Acknowledgements

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